



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>5</sup> :</b> <b>B01J 20/20</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 94/16811</b> <b>(43) International Publication Date:</b> 4 August 1994 (04.08.94)
<b>(21) International Application Number:</b> PCT/US94/00934 <b>(22) International Filing Date:</b> 25 January 1994 (25.01.94) <b>(30) Priority Data:</b> 08/009,778 27 January 1993 (27.01.93) US <b>(71) Applicant:</b> SYRACUSE UNIVERSITY [US/US]; 113 Bowne Hall, Syracuse, NY 13244 (US). <b>(72) Inventors:</b> SCHWARZ, James, A.; 116 Mechanic Street, Fayetteville, NY 13066 (US). PUTYERA, Karol; 491 Euclid Avenue, Syracuse, NY 13210 (US). JAGIELLO, Jacek; 152 Oakland Street, #3, Syracuse, NY 13210 (US). BANDOSZ, Teresa, J.; 152 Oakland Street, #3, Syracuse, NY 13210 (US). <b>(74) Agents:</b> WALL, Thomas, J. et al.; Harris Beach & Wilcox, 217 Montgomery Street, Hills Building, 7th floor, Syracuse, NY 13202 (US).		<b>(81) Designated States:</b> AU, CA, JP, KR, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> ACTIVATED CARBONS MOLECULARLY ENGINEERED  <b>(57) Abstract</b>  A highly microporous adsorbent material is formed as a composite of a natural or synthetic clay or clay-like mineral matrix intercalated with an active carbon. The mineral is prepared and selected to have a selected interlayer spacing between microcrystalline sheets. An organic polymeric precursor is contacted therewith to fill the matrix interstices. Then the precursor is polymerized and carbonized to yield the adsorbent material in which the carbon is intercalated into the mineral matrix. The mineral can be naturally occurring smectite or synthetic hydrotalcite.		

*FOR THE PURPOSES OF INFORMATION ONLY*

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

ACTIVATED CARBONS MOLECULARLY ENGINEEREDBackground of the Invention

This invention relates to active carbon adsorbents and methods of preparing same.

There has been great interest of late in storage media suitable for efficient storage of hydrogen above cryogenic temperatures. Hydrogen has become an increasingly attractive energy source, particularly because of its high energy density per unit weight and because it burns cleanly or can be used directly in fuel cells. Hydrogen is also of interest because it can be produced easily by electrolysis of water. Unfortunately, because hydrogen is highly volatile, storage thereof in sufficient quantities has been a major stumbling block to implementation of a hydrogen-based energy infrastructure. Consequently, great effort has recently been directed towards economical ways to store significant quantities of hydrogen.

Several techniques for storage of hydrogen are discussed in James A. Schwarz U.S. Pat. No. 4,716,736.

Other energy sources, such as methane, have looked attractive but they, too, have presented storage problems for practical use as a secondary energy source.

Recently, it has been observed that carbon adsorbents are much more effective if their pore geometries are related to the molecular dimension of the adsorbate, e.g., hydrogen or methane, and their sorbency is further enhanced if the pores are as uniform in geometry as possible. However, carbon structures have pore formations disposed randomly throughout and the pores tend to have random geometries. Consequently optimal storage of hydrogen, methane, or other gas in active carbon has not been achieved.

Objects and Summary of the Invention:

It is an object to produce a new type of active carbon material capable of enhanced storage of an adsorbate such as hydrogen.

5 It is another object to produce an active carbon adsorbent with pore structure as uniform in geometry as possible.

It is a further object to provide a technique for producing such adsorbent materials, which technique  
10 employs conventional non-exotic materials.

According to an aspect of this invention, a novel method is disclosed of preparing a new type of active carbon adsorbent as a composite material by carbonization of organic compounds intercalated into interlayer spaces  
15 of inorganic porous materials. These inorganic materials are clay or clay-like materials, which can include natural clays such as montmorillonite, or synthetic clay-like materials such as hydrotalcites. These inorganic materials are characterized by a matrix structure wherein  
20 the crystallites are in the form of flat, microscopic sheets. These are separated from one another by pillar-like structures formed of another material which can be an organic anion or a polyoxometallate. The spacings between successive crystallites tend to be rather uniform, so that  
25 the matrix has slit-like pores of uniform geometry.

A polymeric precursor, e.g. of a polystyrene-sulfonate anion, is introduced into the slit-like interstices in the matrix. The polymer is then synthesized within these interstices. This can come about  
30 by reason of the reactive effect of the inorganic materials of the crystallites and or by thermochemical effects.

The ratios of materials, e.g. Mg/Al in the crystallites and in the composition of the pillars can be  
35 selected for a desired charge density and spacing which can have an affect on the resulting carbon product.

Carbonization of the chemically bonded polymer precursor between layers is carried out by a heat treatment, followed by activation of the resultant carbon material.

5           If desired, the clay or clay-like matrix can be removed from the carbon material, e.g. by dissolving it in an inorganic acid or other reagent. The resulting highly porous carbon will be much lighter than the composite material, giving the adsorbent a higher weight-storage  
10           ratio for the hydrogen or other adsorbate.

#### Brief Description of the Drawing

Fig. 1 is a chart of H<sub>2</sub> adsorption vs pressure showing advantageous features of the present invention.

15           Fig. 2 is a chart of adsorption isotherms for an embodiment of this invention.

#### Description of the Preferred Embodiment

A number of adsorbent storage media have been prepared using an inorganic material as a molecular container to provide structural uniformity and structural  
20           integrity to the resulting microporous carbon adsorbent media. Several natural and synthetic materials have been found to be suitable for use as molecular containers. These are generally considered clay or clay-like materials e.g. mixtures of magnesium salts or oxides and aluminum  
25           oxides. These materials are typically characterized by a flat microcrystalline structure, e.g., flat plates or sheets, which are separated by pillars of a suitable material so that the successive sheets are held parallel and separated by slit-like gaps of uniform thickness. A  
30           natural material for this purpose can be a smectite, such as a montmorillonite fraction separated from a Wyoming bentonite clay. A synthetic material for this can be Mg-Al-CO<sub>3</sub> hydrotalcite. The natural materials can be examined by standard known techniques, e.g. x-ray spectroscopy, for  
35           selecting the material to have a predetermined thickness of its slit-like pores. The synthetic hydrotalcites can

have their gaps or pores engineered to a desired thickness by selection of pillar material.

The molecular engineering of these materials is a convenient approach to creation of novel containers for molecular precursors. These can also be used to create composite sorbents which exploit the combined properties of the mineral and the carbon.

Methods for molecular engineering of these composite materials include structural alteration by intercalation of inorganic polyions or modification of their chemical properties by incorporation of organic polymer molecules into their structure.

The method of intercalation involves the introduction of large metal polycations, in the case of smectites, or polyoxometalates, in the case of hydrotalcites, into the interlayer spaces. The polyions can act as "pillars" supporting the layers and rendering their structure rigid. The intercalated structure is characterized by large specific surface area, developed porosity and with interacting surface acido-basic properties.

The structural and chemical properties of the mineral sorbent depend on the method of modification of the initial mineral and on the heat treatments during the processing to obtain a final product.

In one possible embodiment, hydroxy-aluminum oligocations were introduced into the interlayer spaces of montmorillonite separated from a Wyoming bentonite. This material was calcined at 673 K and then saturated by polyfurfuryl alcohol which was polymerized/carbonized between the silicate layers. Hydrotalcite, with a similar layer structure, but opposite acido-basic surface properties, was synthesized and its chemical structure modified by incorporation of 4-styrenesulfonate anions between its layers followed by polymerization/carbonization.

## Examples

### Example I

Intercalated samples were prepared from Wyoming bentonite according to known separation techniques. Briefly, the montmorillonite fraction was saturated with 1 N NaCl to obtain Na-montmorillonite for ion exchange with hydroxy-aluminum cations. Two different samples were chosen for further study; they are designated as M (sodium form) and MA (hydroxy-aluminum montmorillonite heat treated at 673K for 10 hours).

Smectite-furfuryl alcohol complexes were prepared by placing dry Na-montmorillonite M and MA into 20% solutions of furfuryl alcohol (FA) in benzene. The mixture was stirred under a nitrogen atmosphere for three days at room temperature. The samples were then washed with pure benzene to remove FA adsorbed on the outer surface of smectite. The polymerization of furfuryl alcohol between the layers was carried out by heating the samples under a nitrogen flow at 353 K for 24 hours and then at 423 K for 6 hours. The samples of minerals with polymer in the interlayer space were heated-treated at 973 K for 3 hours under a nitrogen flow in order to carry out the carbonization reaction.

### Example II

Synthetic Mg-Al-CO<sub>3</sub> hydrotalcite was prepared by the reaction of an aqueous sodium aluminate solution with a stoichiometric amount of basic magnesium carbonate 4MgCO<sub>3</sub>Mg(OH)<sub>2</sub>.5H<sub>2</sub>O. The reaction was carried out using two different Mg/Al ratios, namely 3:1 and 2:1.

The interlayer space in these minerals, i.e., a hydrotalcite-like structure, provides a reactive environment. The weakness of bonding between layers allows for introduction of different anions and formation of intercalation compounds with organic and organometallic, silicate, and polyoxometalate compounds. Polyoxometalate ions introduced as pillars increase the

thermal stability of these materials and after calcination they display high values of surface area. The following Table lists examples of pillared polyanions and organic compounds.

ORGANIC ANIONS	POLYOXOMETALATES
terephthalate	$[Mo_7O_{24}]^{6-}$
p-toluenesulfonate	$[V_{10}O_{28}]^{6-}$
dihydroxy-benzenedisulfonate	$[PMo_6V_6O_{40}]^{5-}$
naphtalenedisulfonate	$[PMo_6W_6O_{40}]^{3-}$
styrenesulfonate	$[PMo_{12}O_{40}]^{3-}$
polystyrenesulfonate	$[Ta_6O_{18}(OH)]^{7-}$
	$[Nb_6O_{18}(OH)]^{7-}$
	$[PW_{12}O_{40}]^{3-}$
	$[H_2W_{12}O_{40}]^{5-}$

5           The reaction mixture was prepared as follows:  
 37.34g (384 mmol  $Mg^{2+}$ ) or 24.87g (256 mmol  $Mg^{2+}$ ) of  
 magnesium salt was added continuously to an aqueous  
 solution of  $Na[Al(OH)_4]$ , prepared by dissolution of 10g  
 $Al(OH)_3 \cdot nH_2O$  (128 mmol  $Al^{3+}$ ) in 60 ml of 50% NaOH. The  
 10 former resulted in the 3:1 and the latter in the 2:1 Mg/Al  
 ratios. The suspension was stirred at 303 K for 6 hours,  
 and then the reaction mixture was heated to 358 K and  
 continuously stirred at this temperature for 18 hours.  
 The hydrotalcite thus formed was then separated by  
 15 centrifugation and washed thoroughly with deionized water  
 to remove the sodium ions. It was then dried for 24 hours  
 at 373 K.

          The 4-styrenesulfonate anion was incorporated  
 between the layers of hydrotalcite by standard methods.  
 20 Accordingly, the mixed magnesium-aluminum oxide solid  
 solution prepared by calcination of carbonated  
 hydrotalcite was hydrothermally reconstructed to pure and  
 crystalline organic derivatives of hydrotalcite through  
 the meixnerite phase. Thus, 5g of the initial Mg-Al- $CO_3$   
 25 hydrotalcite was first calcined for 3 hours at 723 K, and  
 then this calcined product was placed into 100 ml of a 1:1  
 (by volume) water ethylene glycol solution. The



suspension was then aged for 24 hours at 338 K under a nitrogen atmosphere. After this treatment, the formed OH intercalate (meixnerite) in the presence of the organic salt sodium-4-styrenesulfonate, in stoichiometric ratio, was transformed into the hydrotalcite-type structure of the corresponding anion. To achieve crystalline products, the transformation process was carried out at 338 K for 36 hours. The 4-styrenesulfonate anion in the interlayer spaces of hydrotalcite was polymerized in 0.1 M aqueous solution of potassium persulfate at 358 K. Carbonization of the intercalated polymer was carried out in a flow of nitrogen at 823 K for 3 hours.

It has been observed that the surface free energy values of the minerals are affected by the modification process, although for both natural and synthetic minerals the surface acidity of the final product after introduction of polymers and carbonization is virtually unchanged as compared with initial values.

High values of surface free energy,  $\Delta G_{CH_2}$ , appear to be a characteristic of the carbon-mineral composites. Such high values for microporous carbon can be explained based on the fact that the adsorption potential for the adsorbate gas (e.g.  $H_2$  or  $CH_4$ ) is strongly enhanced in the slit-like micropores.

Various carbon mineral composite adsorbents have been prepared and examined, and these have had an interlayer space between about 0.26 nm to 0.70 nm in the case of adsorbents of Example I, or between about 0.28 and 1.53 nm in the case of hydrotalcites of Example II. The modification process of intercalation, polymerization, and calcination causes small increases or decreases in the interlayer distance. Generally, for synthetic hydrotalcites, carbonization leads to a small increase in the interlayer distance as compared with their initial forms.

The composite mineral-carbon media can be used as storage media with excellent adsorption properties for a target adsorbate and also with high structural strength and integrity. However, the mineral component can be removed by dissolution in a strong acid such as HCl or HF, leaving the microporous carbon. This adsorbent medium has high affinity for the target adsorbate, but is extremely light weight.

Because the materials employed are easily available and can be easily handled, large amounts of sorbent material can be economically prepared. This makes the product especially attractive as a storage medium for secondary energy source gases such as hydrogen or methane, where large volumes of the adsorbate are likely to be encountered.

The product material can be employed in a number of other applications as well, such as filtering or membrane separation; fuel cells; as catalytic membrane for aerosol/particulate abatement; as catalyst support e.g. in ammonia synthesis; for conductive polymers; dielectric materials; fuel cell electrodes; or in medical treatments e.g. as selective scavengers of ingested poisons.

In conclusion, we have found that carbonization of chemically bonded polyanions between the layers of hydrotalcite at 550°C (823K) followed by activation of the resultant material under a variety of thermal treatments between 150 and 500°C (423K to 773K), has yielded a calcined mineral matrix/active carbon system with a developed microporosity, and with high adsorption over a range of temperatures and pressures.

Carbonization of polystyrene sulfonate derivatives of hydrotalcite leads to formation of a calcined hydrotalcite matrix and active carbon system with a desirable developed microporosity. The amount of intercalated organic material can be varied to yield, after carbonization, mineral matrix/active carbon systems

with different adsorption characteristics. In particular, the interstitial or interlayer distance in the matrix can be varied to correspond with the desired pore geometry for a given target adsorbate. The adsorption capacity has  
5 been found to increase with the temperature of pretreatment of the calcined mineral matrix-active carbon system.

Fig. 1 shows hydrogen adsorption characteristics of adsorptive medium prepared according to Example I of this  
10 invention, here using a calcined hydroxy aluminum smectite prepared with polyfurfuryl alcohol which is polymerized and then carbonized (upper curve), compared with a control adsorptive medium made of the smectite saturated with polyfurfuryl alcohol and then carbonized (lower curve).  
15 The threefold increase in absorptivity is believed to come about from the chemical events occurring during processing of the alcohol in the uniform slit-like micropores.

Fig. 2 shows adsorptive curves of a synthetic hydrotalcite based adsorption medium for CO<sub>2</sub>. Here, a  
20 chemically bonded polyanion, namely poly(4-styrene sulfonate) was formed between layers of magnesium/aluminum based crystallites, and carbonized at about 823 K to yield a calcined hydrotalcite activated carbon system, with developed microporosity. Adsorption was measured at 5°C  
25 (278 K), 25°C (298 K), and 40°C (313 K). The isosteric heat of adsorption was found to be 34 KJ/mol, a value whose magnitude is consistent with adsorption in small micropores.

From these data it can be concluded that  
30 carbonization of polystyrene sulfonate derivative of hydrotalcite leads to the formation of microporous calcined hydrotalcite/active carbon systems. The conclusion that this system is microporous is based on a comparison of the isothermic heats of adsorption of CO<sub>2</sub> on  
35 the materials known to be microporous (e.g., Zeolite A 43 KJ/mol, BPL carbon 25 KJ/mol).

The invention has been described here with reference to a few illustrative examples. However, the invention is not limited to those examples. Rather, many modifications and variations thereof would present  
5 themselves to those of skill in the art without departure from the principles of this invention, as defined in the appended claims.

We Claim:

1           1.     A microporous carbon adsorbent material  
2     comprising an inorganic matrix and active carbon supported  
3     within said matrix, wherein said matrix is a pillared clay  
4     or a pillared clay-like material in the form of  
5     microscopic sheets separated from one another by pillars  
6     of a suitable material to define slit-like interstices  
7     therebetween, and said active carbon is intercalated  
8     between said sheets of said matrix.

1           2.     The microporous carbon adsorbent of claim 1  
2     wherein said matrix is in the form of a natural clay  
3     material.

1           3.     A microporous carbon adsorbent material  
2     comprising an inorganic matrix and active carbon supported  
3     within the matrix, where said matrix is formed of  
4     synthetic hydrotalcite layered structures in the form of  
5     microscopic sheets separated from one another by pillars  
6     of a suitable material to define slit-like interstices  
7     therebetween, and said active carbon is intercalated  
8     between said sheets of said material.

1           4.     A process of forming a microporous active  
2     carbon adsorbent, comprising the steps of preparing a  
3     matrix of a pillared clay or clay-like inorganic material  
4     in the form of microscopic sheets separated from one  
5     another by pillars of another suitable material to define  
6     slit-like interstices between successive ones of said  
7     sheets; contacting said matrix with an organic polymeric  
8     precursor so that the interstices in the matrix are filled  
9     with the precursor; and carbonizing said organic precursor  
10    within the slit-like interstices of said matrix to yield  
11    the adsorbent in which the carbon is intercalated into the  
12    interstices of the organic matrix as said microporous  
13    active carbon adsorbent.

1           5. The process of claim 4 wherein said preparing  
2 the matrix includes selecting a suitable clay-or clay-like  
3 inorganic material wherein said interstices are of  
4 substantially uniform width, selected to be as near a  
5 predetermined desired width as possible.

1           6. The process of claim 4 wherein said preparing  
2 the matrix includes forming said matrix of a synthetic  
3 hydrotalcite layered structure and separating sheets  
4 thereof with pillars of a suitable material to form said  
5 interstices as uniform as possible and of a selected  
6 predetermined width.

1           7. The process of claim 4, wherein said  
2 carbonizing is carried out by treating said precursor to  
3 form a polymer thereof within said interstices; and then  
4 calcining said polymer to yield said active carbon.

1           8. A process of forming a microporous active  
2 carbon adsorbent, comprising the steps of  
3           preparing a matrix of a pillared clay or clay-like  
4 inorganic material in the form of microscopic sheets  
5 separated from one another by pillars of another suitable  
6 material to define slit-like interstices between  
7 successive ones of said sheets;  
8           contacting said matrix with an organic polymeric  
9 precursor so that the interstices in the matrix are filled  
10 with said precursor;  
11           carbonizing said organic precursor within the slit-  
12 like interstices of said matrix to produce a structure in  
13 which the carbon is intercalated into the interstices of  
14 the organic matrix; and  
15           removing the matrix from the active carbon to yield  
16 said adsorbent in the form of active carbon microscopic  
17 sheets defining therebetween slit-like micropores of a  
18 predetermined, substantially uniform width.

1           9. The process of claim 8 wherein said removing is  
2 carried out by dissolving the inorganic matrix is an  
3 inorganic reagent.

10. A microporous carbon adsorbent material which  
consists essentially of microscopic sheets of active  
carbon spaced from one another to define therebetween  
slit-like micropores of a predetermined, substantially  
uniform width.

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 5 B01J20/20

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 5 B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,1 610 408 (W. BURNHAM ALEXANDER) 14 December 1926 see page 1, line 1-78 ---	1,2
A	DE,C,286 428 (MALACAPIT-GES.) 14 May 1912 see page 2, column 11-40 ---	1,2
A	CARBON vol. 26, no. 4, 1988 pages 573 - 578 NAOHIRO SONOBE 'CARBONIZATION OF POLYACRYLONITRILE IN A TWO-DIMENSIONAL SPACE BETWEEN MONTMORILLONITE LAMELLAE' " IN TOTALITY " ---	1,2,4,5, 7-10
A	US,A,4 458 030 (MANABE) 3 July 1984 see column 6-8; claims 1-5 --- -/--	1-3

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

## \* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

31 May 1994

Date of mailing of the international search report

10.06.94

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentaan 2  
NL - 2280 HV Rijswijk  
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+ 31-70) 340-3016

Authorized officer

Wendling, J-P



## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB,A,2 035 282 (SHANDON SOUTHERN PRODUCTS) 18 June 1980 see page 5; claims 1-20 ---	1,4,8,9
A	US,A,4 732 887 (OBANAWA) 22 March 1988 see column 29-30; claims 1-16 ---	1,8,9
A	DE,C,337 060 (REKORD-CEMENT-IND.) 2 October 1917 ---	
A	DE,A,40 15 555 (AFFONSO BETTINA) 21 November 1991 see column 1; claims 1-3 -----	1,2

## INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US 94/00934

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-1610408		NONE	
DE-C-286428		NONE	
US-A-4458030	03-07-84	JP-A- 58214338	13-12-83
GB-A-2035282	18-06-80	DE-A,C 2946688 US-A- 4263268	12-06-80 21-04-81
US-A-4732887	22-03-88	JP-A- 61090710 JP-A- 61091082 AU-B- 578315 AU-A- 4844485 DE-A,C 3536397 FR-A- 2571628 GB-A,B 2168045	08-05-86 09-05-86 20-10-88 17-04-86 17-04-86 18-04-86 11-06-86
DE-C-337060		NONE	
DE-A-4015555	21-11-91	DE-A- 5919567	20-12-90

**PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>5</sup> :</b> <b>B01J 20/20</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 94/16811</b> <b>(43) International Publication Date:</b> 4 August 1994 (04.08.94)
<b>(21) International Application Number:</b> PCT/US94/00934 <b>(22) International Filing Date:</b> 25 January 1994 (25.01.94)  <b>(30) Priority Data:</b> 08/009,778      27 January 1993 (27.01.93)      US  <b>(71) Applicant:</b> SYRACUSE UNIVERSITY [US/US]; 113 Bowne Hall, Syracuse, NY 13244 (US).  <b>(72) Inventors:</b> SCHWARZ, James, A.; 116 Mechanic Street, Fayetteville, NY 13066 (US). PUTYERA, Karol; 491 Euclid Avenue, Syracuse, NY 13210 (US). JAGIELLO, Jacek; 152 Oakland Street, #3, Syracuse, NY 13210 (US). BANDOSZ, Teresa, J.; 152 Oakland Street, #3, Syracuse, NY 13210 (US).  <b>(74) Agents:</b> WALL, Thomas, J. et al.; Harris Beach & Wilcox, 217 Montgomery Street, Hills Building, 7th floor, Syracuse, NY 13202 (US).		<b>(81) Designated States:</b> AU, CA, JP, KR, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i> <i>With amended claims.</i>  <b>Date of publication of the amended claims:</b> 1 September 1994 (01.09.94)
<b>(54) Title:</b> ACTIVATED CARBONS MOLECULARLY ENGINEERED  <b>(57) Abstract</b>  A highly microporous adsorbent material is formed as a composite of a natural or synthetic clay or clay-like mineral matrix intercalated with an active carbon. The mineral is prepared and selected to have a selected interlayer spacing between microcrystalline sheets. An organic polymeric precursor is contacted therewith to fill the matrix interstices. Then the precursor is polymerized and carbonized to yield the adsorbent material in which the carbon is intercalated into the mineral matrix. The mineral can be naturally occurring smectite or synthetic hydrotalcite.		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

## AMENDED CLAIMS

[received by the International Bureau on 2 August 1994 (02.08.94);  
original claims 1-4 and 6-10 amended; original claim 5 deleted (3 pages)]

1           1.     A microporous carbon adsorbent material  
2     comprising an inorganic matrix and active carbon supported  
3     within said matrix, wherein said matrix is a pillared  
4     natural or synthetic clay material in the form of layers  
5     spaced from one another by pillars of an inorganic  
6     pillaring material that is selected to define slit-like  
7     microporous interstices therebetween molecularly engi-  
8     neered with a pore size that corresponds to a given target  
9     adsorbate, and said active carbon is intercalated between  
10    said layers of said matrix.

1           2.     The microporous carbon adsorbent of claim 1  
2     wherein said matrix is in the form of a natural clay  
3     material.

1           3.     A microporous carbon adsorbent material  
2     comprising an inorganic matrix and active carbon supported  
3     within the matrix, where said matrix is formed of  
4     synthetic hydrotalcite layered structures in the form of  
5     layers spaced from one another by pillars of an inorganic  
6     pillaring material that is selected to define slit-like  
7     microporous interstices therebetween, the interstices  
8     being molecularly engineered to have a pore size that  
9     corresponds to a given target adsorbate, and said active  
10    carbon is intercalated between said layers of said  
11    material.

1           4.     A process of molecularly engineering a  
2     microporous active carbon adsorbent to have slit-like  
3     micropores whose size corresponds to a given target  
4     adsorbate, comprising the steps of preparing a matrix of  
5     a pillared inorganic natural or synthetic clay material in  
6     the form of layers spaced from one another by pillars of  
7     an inorganic pillaring material to define slit-like  
8     microporous interstices between successive ones of said

9 layers, the interstices being molecularly engineered to  
10 have said pore size that corresponds to said given target  
11 adsorbate; contacting said matrix with an organic  
12 polymeric precursor so that the interstices in the matrix  
13 are filled with the precursor; and carbonizing said  
14 organic precursor within the slit-like interstices of said  
15 matrix to yield the adsorbent in which the carbon is  
16 intercalated into the interstices of the inorganic matrix  
17 as said microporous active carbon adsorbent.

1 6. The process of claim 4 wherein said preparing  
2 the matrix includes forming said matrix of a synthetic  
3 hydrotalcite layered structure and separating layers  
4 thereof with pillars to form said interstices of a  
5 selected uniform width.

6 7. The process of claim 4, wherein said carboniz-  
7 ing is carried out by treating said precursor to form a  
8 polymer thereof within said interstices; and then  
9 calcining said polymer to yield said active carbon.

1 8. A process of molecularly engineering a  
2 microporous active carbon adsorbent, comprising the steps  
3 of:

4 preparing a matrix of a pillared natural or  
5 synthetic inorganic clay material in the form of layers  
6 spaced from one another by pillars of an inorganic  
7 pillaring material that is selected to define slit-like  
8 microporous interstices between successive ones of said  
9 sheets, such that the interstices are molecularly  
10 engineered to have a pore size that corresponds to a given  
11 target adsorbate;

12 contacting said matrix with an organic polymeric  
13 precursor so that the interstices in the matrix are filled  
14 with said precursor;

15 carbonizing said organic precursor within the slit-  
16 like interstices of said matrix to produce a structure in  
17 which the carbon is intercalated into the interstices of  
18 the inorganic matrix; and  
19 removing the matrix from the active carbon to yield  
20 said adsorbent in the form of active carbon layers  
21 defining therebetween slit-like micropores of a substan-  
22 tially uniform and preselected width that corresponds to  
23 said target adsorbate.

1 9. The process of claim 8 wherein said removing is  
2 carried out by dissolving the inorganic matrix in an  
3 inorganic reagent.

1 10. A microporous carbon adsorbent material  
2 prepared by the process of claim 8 which consists  
3 essentially of microscopic sheets of active carbon spaced  
4 from one another to define therebetween slit-like  
5 micropores of a substantially uniform preselected width  
6 that is molecularly engineered such that interstices  
7 between said sheets correspond to a given target adsor-  
8 bate.